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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>H01L 21/00, B44C 1/22, C09G 1/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/53532</b> <b>(43) International Publication Date:</b> 21 October 1999 (21.10.99)
<b>(21) International Application Number:</b> PCT/US99/07482 <b>(22) International Filing Date:</b> 5 April 1999 (05.04.99)  <b>(30) Priority Data:</b> 09/058,618 10 April 1998 (10.04.98) US 09/277,454 26 March 1999 (26.03.99) US  <b>(71) Applicant:</b> FERRO CORPORATION [US/US]; 1000 Lakeside Avenue, Cleveland, OH 44114 (US).  <b>(72) Inventors:</b> PRENDERGAST, John, E.; 45 South Kashong Drive, Geneva, NY 14456 (US). HER, Yieshein; 3430 West Lake Road, Canandaigua, NY 14424 (US). BABU, Suryadevara, V.; 24 Haggerty Road, Potsdam, NY 13676 (US). LI, Yuzhuo; 55 Pine Street, Potsdam, NY 13676 (US). HARIHARAPUTHIRAN, Mariappan; Apartment 34, 43 Market Street, Potsdam, NY 13676 (US).  <b>(74) Agent:</b> CLARK, Kenneth, A.; Rankin, Hill, Porter & Clark LLP, Suite 700, 925 Euclid Avenue, Cleveland, OH 44115-1405 (US).		<b>(81) Designated States:</b> CA, JP, KR, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SLURRY FOR CHEMICAL-MECHANICAL POLISHING METAL SURFACES  <b>(57) Abstract</b> <p>The present invention provides a slurry for chemical-mechanical polishing metal surfaces which significantly increases the removal rate and is capable of polishing metals which are inert to most common oxidizing agents. The slurry is particularly useful for polishing metal layers on semiconductor wafer substrates. The slurry includes water, abrasive particles, and an oxidizing solution. In one preferred embodiment, the oxidizing solution comprises one or more water soluble peroxides, one or more amino acids, and one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium, with copper being preferred. In another preferred embodiment, the oxidizing solution comprises one or more water soluble peroxides, one or more organic amines, and optionally one or more metals and/or compounds containing metals.</p>		

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Title: **SLURRY FOR CHEMICAL-MECHANICAL  
POLISHING METAL SURFACES**

**Background Of The Invention**

**Field of the Invention**

The present invention concerns chemical compositions for use in polishing. The present invention relates to a polishing slurry for the chemical-mechanical polishing of metal surfaces.

**Description of the Related Art**

Chemical-mechanical polishing ("CMP") is a technology which has its roots in the pre-industrial era. In recent years, CMP has become the technology of choice among semiconductor chip fabricators to polish or planarize the surface of semiconductor chips after each metal containing circuit pattern layer is laid down. CMP technology is well-known, and is typically accomplished by applying pressure with a polishing pad saturated with a metal polishing slurry to the surface to be polished.

Examples of prior art patents that concern CMP include U.S. Patent No. 4,959,113 issued to Roberts that discloses a slurry for CMP metal surfaces which generally comprises: (i) water; (ii) abrasive particles; and (iii) a salt. U.S. Patent No. 5,354,490 issued to Yu et al. discloses a slurry for the CMP of predominantly copper metal surfaces which generally comprises: (i) water; (ii) abrasive particles; and (iii) a component selected from the group consisting of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{AgNO}_3$ . U.S. Patent No. 5,527,423 issued to Neville et al. discloses a slurry for CMP metal surfaces which generally comprises: (i) water; and (ii) high

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purity fine metal oxide particles. Additionally, U.S. Pat. 5,575,885 issued to Hirabayashi et al. discloses a slurry for CMP copper-based metal surfaces which generally comprises: (i) water; (ii) an organic acid; and (iii) an oxidizer.

Unfortunately, many prior art slurries for CMP metal surfaces have achieved less than desired removal rates. Moreover, many prior art slurries for CMP metal surfaces have not been particularly useful for polishing metals, such as tantalum, which are inert to common oxidizing agents. Accordingly, a slurry for CMP metal surfaces is needed which provides significant improvement in terms of removal rates as compared to the prior art slurries. Moreover, a slurry for CMP metal surfaces is needed which is useful for polishing metals which are inert to common oxidizing agents.

#### Summary Of The Invention

The present invention is directed to a chemical composition or slurry for CMP which displays superior removal rate when polishing metal surfaces, including metal surfaces which are inert to common oxidizing agents. A slurry for CMP metal surfaces according to the present invention generally comprises: (i) water; (ii) abrasive particles; and (iii) an oxidizing solution. In one preferred embodiment, the oxidizing solution (iii) comprises: (a) water soluble peroxide; (b) one or more amino acids; and (c) one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium, with copper being preferred. The use of metals and/or compounds containing metals in combination with water soluble peroxide

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and amino acid results in the accelerated generation of hydroxyl radicals and yields a much more effective polishing composition.

In another preferred embodiment, the oxidizing solution (iii) comprises: (a') water soluble peroxide; and (b') organic amine. The use of organic amine in combination with water soluble peroxide also results in the accelerated generation of hydroxyl radicals. To further increase the generation of hydroxyl radicals, such oxidizing solution can further optionally comprise one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium, with copper being preferred.

These and other aspects and advantages of the present invention will be readily understood and appreciated by those skilled in the art from the following detailed description of the invention with the best mode contemplated for practicing the invention in view of the accompanying drawings.

#### **Brief Description Of The Drawings**

In the annexed drawings:

FIG. 1 is a graph illustrating that in a slurry of the present invention the rapid formation of hydroxyl radicals occurs when hydrogen peroxide, glycine and copper nitrate are present at the same time;

FIG. 2 is a graph illustrating that in a slurry of the present invention the rate of hydroxyl radical formation varies when other amino acids are substituted for glycine:

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FIG. 3 is a graph illustrating that in a slurry of the present invention the rate of hydroxyl radical formation varies when elemental copper or copper oxide are substituted for copper nitrate; and

FIG. 4 is a graph illustrating that in a slurry of the present invention the use of copper nitrate, hydrogen peroxide and glycine in the slurry increases the polish rate of copper.

#### Detail Description Of The Preferred Embodiments

The present invention provides a chemical composition for use as a CMP slurry which provides high removal rates when polishing metal surfaces. The slurry contains: (i) water; (ii) abrasive particles; and (iii) an oxidizing solution. In one preferred embodiment, the oxidizing solution (iii) comprises: (a) water soluble peroxide; (b) an amino acid or mixture of amino acids; and (c) one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium, with copper being preferred. The combination of components (a), (b) and (c) generates a large amount of hydroxyl radicals ( $\text{OH}\cdot$ ), which is a much stronger oxidizing agent as compared to hydrogen peroxide alone. In another preferred embodiment, the oxidizing solution (iii) comprises: (a') water soluble peroxide; and (b') organic amine. The combination of components (a') and (b') also generate a large amount of hydroxyl radicals. Applicants have found that the presence of a stronger oxidizing agent significantly improves the removal rate when polishing metal surfaces.

The water (i) used in the slurry is preferably distilled water. More preferably, the water is doubly distilled water.

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The abrasive particles (ii) used in the slurry may comprise any one or a mixture of a variety of abrasive particles that are conventionally utilized in CMP slurries. Examples of suitable abrasive particles include alumina, silica, silicon nitride, silicon carbide, ceria, copper oxide, iron oxide, nickel oxide, manganese oxide, tin oxide, titania, titanium carbide, tungsten oxide, yttria and zirconia, or a combination thereof. The abrasive particles preferably have a mean size ranging from about 0.02 to about 1.0 micrometers, with a maximum size of less than about 10 micrometers. The abrasive particles are preferably present in the slurry in an amount of from about 0.1 to about 60% by weight of the slurry.

The oxidizing solution (iii) used in the slurry must rapidly generate more hydroxyl radicals than would otherwise be generated by hydrogen peroxide alone. The applicants have found that the presence of a relatively large concentration of hydroxyl radicals greatly enhances the polishing rate of metals, including metals such as tantalum which are inert to most oxidizing agents. In one preferred embodiment, the oxidizing solution (iii) comprises: (a) one or more water soluble peroxides; (b) an amino acid or mixture of amino acids; and (c) one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium, with copper being preferred. In another preferred embodiment, the oxidizing solution (iii) comprises: (a') one or more water soluble peroxides; (b') one or more organic amines; and optionally (c') one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium, with copper being preferred.

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The water soluble peroxide (iii)(a) and (iii)(a') may comprise any water soluble peroxide having the structure  $R-O-O-H$ , where R is hydrogen, an aliphatic hydrocarbon, or an aromatic hydrocarbon. In the most preferred embodiment, the water soluble peroxide is hydrogen peroxide. In another preferred embodiment, the water soluble peroxide is t-butylhydroperoxide. The water soluble peroxide is preferably present in the slurry by weight from about 0.1% to about 30%.

The amino acid (iii)(b) is selected from amino carboxylic acid, amino alkyl carboxylic acid, amino phenyl carboxylic acids and the sodium, potassium, and ammonium salts thereof, or a combination of the foregoing. Examples of specific amino acids suitable for use in the present invention include arginine, cysteine, glutamine, glutamic acid, glycine, histidine, phenylalanine, and serine. The amino acid is preferably present in the slurry in an amount of from about 0.1 to about 10% by weight.

The metals and/or compounds containing metals (iii)(c) and optionally (iii)(c') are one or more selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium. The metals can be used in the elemental form or in the form of metal containing compounds, such as water-soluble salts and oxides which are preferred. Copper is the most preferred metal. Suitable forms of copper for use in the invention include, for example, copper acetate, copper bromide, copper butyrate, copper chlorate, copper chloride, copper citrate, copper fluoride, copper formate, copper gluconate, copper glycinate, copper hexafluorosilicate, copper nitrate, copper oxide powder, copper hydroxide powder, elemental copper powder, copper perchlorate, copper phenolsulfonate,



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copper salicylate, copper selenate, copper sulfate, and copper tartrate, or a combination of the foregoing. Similar forms of chromium, cobalt, iron, lead, nickel, palladium, rhodium, samarium, and scandium would also be suitable for use in the invention. The metals and/or compounds containing metals are preferably present in the slurry in an amount of from about 0.1% to about 10% by weight.

The organic amine (iii)(b') used in the slurry may comprise primary amine ( $\text{RNH}_2$ ), secondary amine ( $\text{R}_2\text{NH}$ ), tertiary amine ( $\text{R}_3\text{N}$ ), mixtures thereof, and/or an amine containing all or some of these three types of amine moieties, where R is an aliphatic hydrocarbon or an aromatic hydrocarbon. In the currently preferred embodiment, the organic amine is bis(hexamethylene)triamine ( $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}(\text{CH}_2)_6\text{NH}_2$ ). The organic amine is preferably present in the slurry in an amount of from about 0.1% to about 10% by weight.

The slurry according to the present invention effectively polishes metals throughout a wide pH range. For semiconductor polishing applications, it is generally preferred to polish the metal layers deposited on the substrate rapidly without etching or polishing the substrate material at all. It has been found that polishing with a slurry having a pH greater than about 7 will sometimes cause the substrate material to become polished or etched. However, when the pH of the slurry is adjusted such that it is more acidic, the substrate material will not become polished or etched. Accordingly, for such applications the slurry is optionally adjusted to a pH of from about 2 to about 5 by adding common acids such as hydrochloric acid, nitric acid, sulfuric acid, acetic acid, phosphoric acid or other conventional acids.

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The slurry or polishing composition should be formulated so as to give a polishing slurry having a desirable concentration and viscosity. The desirable viscosity range should be low enough such that the polishing composition is free flowing. Additives such as ethylene glycol, nitric acid, potassium hydroxide and propylene glycol may be added to adjust the viscosity of the slurry. In order to stabilize the polishing slurry against settling, flocculation and decomposition of the oxidizing component, a variety of additives, such as, for example, surfactant, polymeric stabilizers or other surface active dispersing agents can be used.

Another aspect of the present invention relates to a method for polishing a metal surface comprising the steps of providing a polishing slurry composition, contacting the polishing slurry composition with a metal surface to be polished and polishing the metal surface. In this method the polishing slurry composition comprises water, abrasive particles, and an oxidizing solution. In one embodiment, the oxidizing solution comprises one or more water soluble peroxides, one or more amino acids, and one or more metals or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium. In another embodiment, the oxidizing solution comprises one or more water soluble peroxides, one or more organic amines, and optionally one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium. Thus, the method uses the slurry discussed above.

The polishing method of the present invention is carried out by contacting the aqueous polishing composition or slurry with the metal to be polished, normally at room temperature.

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The metal surface is then polished with the composition using a felt or other polishing pad. Typical pads include Rodel Suba 500 pads; IC 1000 pads or similar commercially available pads. Although polishing is usually conducted at room temperature, it will be appreciated that an increase in the temperature generally results in an increase in the concentration of hydroxyl radicals formed.

In addition to providing a slurry, the polishing composition of the present invention may be generated in situ. More particularly, for example, the metals and/or compounds containing metals (iii)(c) and the amino acids (iii)(b) could be added on the metal surface to be polished to a solution of water (i), abrasive particles (ii), and water soluble peroxide (iii)(a). Alternatively, for example, a solution of the metals and/or compounds containing metals (iii)(c), amino acids (iii)(b), and water soluble peroxide (iii)(a) could be added on the polishing surface to a solution of water (i) and abrasive particles (ii). It will be appreciated that since the order of addition is not per se critical, any number of a multitude of possible combinations for forming the slurry in situ could be employed. However, because peroxides decompose rapidly once being mixed with the other components, it is preferable to keep peroxides from the other components in the slurry formulation until immediately prior to use.

In another aspect of the present invention the polishing slurry of the present invention may be formed by incorporating a portion of the components of the slurry in a polishing pad. For example, the amino acids (iii)(b), abrasive particles (ii) and the metals and/or compounds containing metals (iii)(c) could be incorporated directly in the polishing pad, and a solution of water (i) and water soluble peroxide (iii)(a) could then be added at the polishing surface

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to form the polishing slurry in situ. It will be appreciated that the components of the polishing slurry composition according to the invention could be combined in various ways to form the slurry in situ.

5 Pads that contain one or more components of the polishing slurry are well-known, such as the pad disclosed in Mayton et al. U.S. Patent No. 5,000,761 and Shukla et al. U.S. Patent No. 4,576,612. Mayton et al. U.S. Patent No. 5,000,761 and Shukla et al. U.S. Patent No. 4,576,612 are incorporated herein by reference for their teachings of how to produce a pad containing one or more components that serve to form the polishing slurry in situ during the polishing operation.

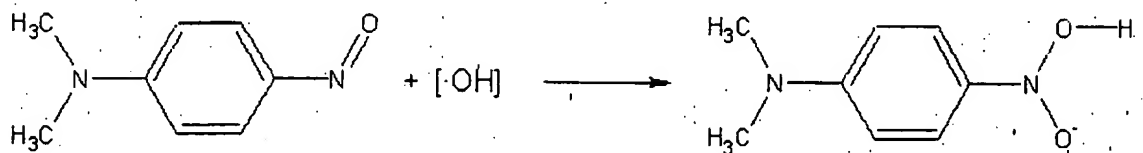
10 The CMP slurry provided herein is particularly useful for polishing metal layers on semiconductor wafer substrates. Metal layers which may be polished using the CMP slurry disclosed herein include aluminum, copper, tantalum, tantalum nitride, titanium, tungsten, titanium nitride, titanium tungsten, and alloys or mixtures thereof.

15 The slurry of the present invention may be prepared in a conventional manner by merely mixing the various components of the formulation. No special mixing techniques or equipment are required, and the order of addition is not critical. The components are preferably combined immediately prior to use.

The present invention will now be described in more detail with reference to the following specific nonlimiting examples.

Preface to Examples

As noted by Liu, X., DiLabi, G.A., Martin, F., and Li, Y in "Catalytic Formation of Hydroxyl Radical from Hydrogen Peroxide in the Presence of an Amine", submitted to J.A.O.S. in 1998, the formation of hydroxyl radicals can be quantitatively analyzed using a hydroxyl radical trap such as N,N-dimethyl-4-nitrosoaniline (PNDA). As the hydroxyl radical is formed, it adds to the PNDA via the reaction described below:



PNDA has a unique and strong absorption in the visible region at 440 nm whereas the product of the reaction between PNDA and a hydroxyl radical has a weak absorption at 440nm. Thus, the amount of hydroxyl radical formed is detected by the disappearance of PNDA over time as indicated by subsequent decreasing absorptions at 440nm.

The concentration of hydroxyl radical can be calculated by the rate equation:

$$-\text{d}[\text{PNDA}]/\text{dt} = k'[\text{PNDA}][\cdot\text{OH}]$$

When assuming  $[\cdot\text{OH}]$  is in steady state, the above-equation becomes:

$$-\text{d}[\text{PNDA}]/\text{dt} = k[\text{PNDA}]$$

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where  $k=k'[\cdot\text{OH}]$ , and  $k'$  is  $1.25 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .  $k$  is a psuedo first order rate constant and consequently the slope of  $\ln([\text{PNDA}]/[\text{PNDA}]_0)$  vs time where  $[\text{PNDA}]_0$  is the original concentration of PNDA.

If the conversion of PNDA is near to completion, the absorption of the product of the reaction between PNDA and a hydroxyl radical at 440nm cannot simply be ignored. The overall absorption at 440nm should then be expressed as a combined contribution from PNDA and PNDA-OH product:

$$A = \epsilon_1 c_1 + \epsilon_2 c_2$$

where  $\epsilon_1$  represents the molar absorptivity of PNDA,  $c_1$  represents the transient concentration of PNDA, and  $l$  is the optical pathlength. Similarly,  $\epsilon_2$  represents the molar absorptivity of the product PNDA-OH, and  $c_2$  represents its corresponding transient concentration.

Considering the fact that, at any given time,  $C_0 = c_1 + c_2$ , then:

$$[\text{PNDA}]/[\text{PNDA}]_0 = [(\epsilon_1/\epsilon_2) - 1]^{-1} \times [(\epsilon_1/\epsilon_2)(A/A_0) - 1]$$

where  $A$  is the absorption of the sample at any given time and  $A_0$  is the initial absorption of the sample.

#### Example 1

The purpose of the series of experiments conducted as Example 1 is to demonstrate the relative strength of various metal ions in combination with glycine in catalyzing the formation of hydroxyl radicals. Accordingly, only simple kinetics need to be used. The slope of  $\ln(A_0/A)$  will be used for the calculation of a steady state concentration of hydroxyl radical.

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The various combinations of components discussed below were tested for their effectiveness in promoting the formation of hydroxyl radical over a thirty minute period. The hydroxyl radical concentration was then calculated for each combination. All percents are by weight unless otherwise stated.

5 In a small vial, 9.0 +/- 0.1 ml doubly distilled H<sub>2</sub>O was added to 0.6 +/- 0.02 ml 30% H<sub>2</sub>O<sub>2</sub>. The solution's pH was regulated to 8.45 +/- 0.05 using small drops of 1N NaOH and 1N H<sub>2</sub>SO<sub>4</sub>. In a separate container, 0.08 +/- 0.01 ml of 5mM PNDA was added to the solution followed immediately by addition of 0.36 +/- 0.02ml of a 5mM metal ion solution of the metals shown in Table 1 below and 0.1% glycine. Each reaction solution's intensity at 10 440nm was measured for 30 minutes in 5 minute intervals at 25°C. Table 1 below sets forth the steady-state hydroxyl radical concentration for each trial as determined using the kinetics equation discussed above.

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Table 1

<u>Ion</u>	<u>Source</u>	<u>Slope of <math>\ln(A_0/A)</math></u>	<u>[·OH] (M)</u>
Cu	copper acetate	0.03590	$2.87 \times 10^{-12}$
Ag	silver nitrate	0.00062	$5.02 \times 10^{-14}$
Al	aluminum nitrate	0.00071	$5.68 \times 10^{-14}$
Co	cobalt nitrate	0.00339	$2.71 \times 10^{-13}$
Cr	chromium chloride	0.00619	$4.95 \times 10^{-13}$
Fe	ferric chloride	0.00201	$1.61 \times 10^{-13}$
Mg	magnesium sulfate	0.00077	$6.16 \times 10^{-14}$
Mn	manganous chloride	0.00036	$2.88 \times 10^{-14}$
Ni	nickelous nitrate	0.00124	$9.92 \times 10^{-14}$
Pb	lead acetate	0.00630	$5.04 \times 10^{-13}$
Ru	ruthenium(III) chloride hydrate	0.00053	$4.24 \times 10^{-14}$
Zn	zinc chloride anhydrous	0.00071	$5.68 \times 10^{-14}$
Pd	palladium(II) nitrate hydrate	0.00352	$2.90 \times 10^{-13}$
Sn	stannous chloride	0.00028	$2.24 \times 10^{-14}$
Sm	samarium dichloride	0.00135	$1.08 \times 10^{-13}$
Cd	cadmium chloride	0.00081	$6.48 \times 10^{-14}$
Fe <sup>2+</sup>	iron(II) sulfate	0.00554	$4.43 \times 10^{-13}$
Pt	potassium chloroplatinate	0.00101	$8.08 \times 10^{-14}$
Cu <sup>2+</sup>	cupric chloride	0.03220	$2.58 \times 10^{-12}$
Sc	scandium acetate	0.00139	$1.11 \times 10^{-13}$
Rh	rhodium chloride	0.00339	$2.71 \times 10^{-13}$
Rh <sup>2+</sup>	rhodium(II) trifluoroacetate dimer	0.00310	$2.48 \times 10^{-13}$

Table 1 demonstrates that copper (both valences) is far superior as a radical promoter than any other metal ion tested. Copper produces 10 times the amount of hydroxyl radical as most species. Only lead, iron (Fe<sup>2+</sup>), and chromium (Cr<sup>3+</sup>) have any comparable results, and their radical production remains less than five times that of copper. Chromium, cobalt, iron, lead, nickel, palladium, rhodium, samarium, and scandium are less effective in promoting hydroxyl radical than copper, but are still useful for that purpose.



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Example 2

The solutions shown in Table 2 below were prepared according to the procedures set forth in Example 1. Each solution's intensity at 440nm was measured for 30 minutes in 5 minute intervals at 25°C. Table 2 below sets forth the hydroxyl radical concentration for each trial as determined using the kinetics equation discussed above.

Table 2

<u>Components of Trial</u>	<u>Slope of <math>\ln(A_0/A)</math></u>	<u>[·OH] (M)</u>
Cu + 0.1% glycine	0.03590	$2.87 \times 10^{-12}$
0.1% bis(hexamethylene)triamine	0.00264	$2.11 \times 10^{-13}$
Cu + 0.1% bis(hexamethylene)triamine	0.00552	$4.42 \times 10^{-13}$
0.5% bis(hexamethylene)triamine	0.01057	$8.46 \times 10^{-13}$
1.0% bis(hexamethylene)triamine	0.01436	$1.15 \times 10^{-12}$
Fe + 1.0% bis(hexamethylene)triamine	0.01456	$1.16 \times 10^{-12}$
Cr + 1.0% bis(hexamethylene)triamine	0.01385	$1.11 \times 10^{-12}$

Example 2 demonstrates that as the concentration of bis(hexamethylene)triamine approaches 1.0% by weight, it becomes a comparable hydroxyl radical promoter to a 0.1% glycine/Cu<sup>2+</sup> system. Example 2 also demonstrates that the addition of metal ions to a triamine solution sometimes increases the effectiveness of the triamine as a hydroxyl radical promoter.

Example 3

This example demonstrates that each of the components of the invention (i.e., for example, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), glycine (NH<sub>2</sub>CH<sub>2</sub>COOH), and copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>)) have to be present at the same time in order to generate large amounts of hydroxyl radicals (OH·).

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More particularly, different aqueous solutions of the following were prepared:  
(1) hydrogen peroxide only; (2) hydrogen peroxide (2% by weight) and glycine (1% by weight); (3) hydrogen peroxide (2% by weight) and copper nitrate (100 ppm by weight); (4-6) hydrogen peroxide (2% by weight), glycine (1% by weight), and copper nitrate (three concentrations utilized in PPM-parts per million). Then, PNDA was added to the solutions to trap hydroxyl radicals as soon as they are generated.

Fig. 1 shows the plot of the ratio of PNDA concentration remaining in solution versus the original PNDA concentration ( $A/A_0$ ) as a function of time. The data clearly show that rapid formation of hydroxyl radicals, indicated by the rapid reduction in PNDA concentration (i.e.  $A/A_0$ ) in the plot, only occurs when each of the components are present at the same time.

#### Example 4

This example shows that other amino acids besides glycine, when mixed with hydrogen peroxide and copper nitrate, will also cause the rapid formation of hydroxyl radicals.

The experiment in Example 3 was repeated except that glycine in the aqueous solutions was replaced with various other amino acids as indicated in Fig. 2. In all cases, the concentrations of hydrogen peroxide, amino acid and copper nitrate were 2% by weight, 1% by weight and 100 ppm, respectively. More particularly, Fig. 2 illustrates the various reduction rates of PNDA concentration in aqueous solutions containing hydrogen peroxide, copper nitrate, and various amino acids. The reduction rate of PNDA is proportional to the rate of formation of hydroxyl radicals.

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Example 5

This example demonstrates that copper nitrate can be replaced by other copper compounds, such as copper oxide (CuO) and elemental copper (Cu), for the purpose of forming hydroxyl radicals.

5           The same experiment as in Example 3 was again repeated, except that the copper nitrate is replaced by copper oxide powder or elemental copper powder. The concentration of hydrogen peroxide and glycine were 2% by weight and 1% by weight, respectively. The concentration of copper oxide and copper powders varied from 3 mg/10 ml to 10 mg/10 ml. The experiment results, as shown in Fig. 3, demonstrate that fast generation of hydroxyl radicals, as indicated by rapid reduction in PNDA concentration ( $A/A_0$ ), occurs when  
10           hydrogen peroxide, glycine, and copper oxide or element copper are present at the same time.

Example 6

This example shows that removal rate of tantalum (Ta) is significantly increased when polishing with the disclosed slurry formulation.

15           A tantalum disc is polished using a Struers polisher and Suba 500 pad, at a pressure of 6.3 psi, and a rotation speed of 90 rpm. Two CMP slurries were used as follows:

Slurry A contains: (1) 3% by weight alumina abrasive particles with a mean diameter of 0.35 micrometers and maximum diameter of 2.0 micrometers; and  
(2) 5% by weight hydrogen peroxide.

20           Slurry B contains: (1) 3% by weight alumina abrasive particles with a mean diameter of 0.35 micrometers and maximum diameter of 2.0 micrometers; (2)

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5% by weight hydrogen peroxide; (3) 1% by weight glycine; and (4) 1% by weight copper nitrate.

The removal rates, determined by weight loss method, are summarized as follows:

<u>Slurry</u>	<u>Removal Rate (nanometer/min)</u>
A	32.0
B	68.5

#### Example 7

This example shows that removal rate of copper (Cu) is significantly increased when polishing with the disclosed slurry formulation.

A copper disc is polished using Struers polisher and Suba 500 pad at a pressure of 6.3 psi, and a rotation speed of 90 rpm, using aqueous solutions containing (1) 5% by weight hydrogen peroxide; (2) 0.1% by weight glycine; and (3) various concentrations of copper nitrate ranging from 0 to 0.42 mol/liter (M). Figure 4 illustrates the resulting polish rate as a function of copper nitrate concentration, which clearly shows that the polish rate of copper is significantly increased only when copper nitrate, hydrogen peroxide and glycine are present at the same time in the slurry formulation.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and illustrated examples shown and described herein. Accordingly, various modifications may be

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made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

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## What is claimed is:

1. A slurry for chemical-mechanical polishing metal surfaces comprising water, abrasive particles, and an oxidizing solution comprising a water soluble peroxide.
2. The slurry for chemical-mechanical polishing metal surfaces as in claim 1 wherein said abrasive particles are selected from the group consisting of alumina, silica, silicon nitride, silicon carbide, ceria, copper oxide, iron oxide, nickel oxide, manganese oxide, tin oxide, titania, titanium carbide, tungsten oxide, yttria, zirconia, and mixtures thereof.
3. The slurry for chemical-mechanical polishing metal surfaces as in claim 1 wherein said abrasive particles have a mean size ranging from about  $0.02\mu\text{m}$  to about  $1.0\mu\text{m}$  with a maximum size of less than about  $10\mu\text{m}$ .
4. The slurry for chemical-mechanical polishing metal surfaces as in claim 1 wherein said abrasive particles are present in said slurry in an amount of from about 0.1% to about 60% by weight.
5. The slurry for chemical-mechanical polishing metal surfaces as in claim 1 wherein said water soluble peroxide has the structure  $\text{R-O-O-H}$ , where R is hydrogen, an aliphatic hydrocarbon, or an aromatic hydrocarbon.
6. The slurry for chemical-mechanical polishing metal surfaces as in claim 1 wherein said water soluble peroxide is present in said slurry in an amount of from about 0.1% to about 30%.
7. The slurry for chemical-mechanical polishing metal surfaces as in claim 1 wherein said pH of said slurry is within the range of from about 2 to about 5.

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8. The slurry for chemical-mechanical polishing metal surfaces as in claim 1, wherein said oxidizing solution further comprises one or more amino acids and one or more metals or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium.

5 9. The slurry for chemical-mechanical polishing metal surfaces as in claim 8 wherein said amino acids are one or more selected from the group consisting of arginine, cysteine, glutamine, glutamic acid, glycine, histidine, phenylalanine, serine, and mixtures thereof.

10 10. The slurry for chemical-mechanical polishing metal surfaces as in claim 8 wherein said amino acids are one or more selected from the group consisting of amino carboxylic acid, amino alkyl carboxylic acid, amino phenyl carboxylic acids, the sodium, potassium, and ammonium salts thereof, and mixtures thereof.

15 11. The slurry for chemical-mechanical polishing metal surfaces as in claim 8 wherein said amino acids are present in said slurry in an amount of from about 0.1% to about 10% by weight.

20 12. The slurry for chemical-mechanical polishing metal surfaces as in claim 8 wherein said metals and/or compounds containing metals are one or more selected from the group consisting of metal-acetate, metal-bromide, metal-butyrate, metal-chlorate, metal-chloride, metal-citrate, metal-fluoride, metal-formate, metal-gluconate, metal-glycinate, metal-hexafluorosilicate, metal-nitrate, metal-oxide powder, metal-hydroxide powder, elemental

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metal powder, metal-perchlorate, metal-phenolsulfonate, metal-salicylate, metal-selenate, metal-sulfate, metal-tartrate, and combinations thereof.

13. The slurry for chemical-mechanical polishing metal surfaces as in claim 8 wherein said metals and/or compounds containing metals are present in said slurry in an amount of from about 0.1% to about 10% by weight.

14. The slurry for chemical-mechanical polishing metal surfaces as in claim 8 wherein said abrasive particles comprise alumina having a mean diameter of about  $0.35\mu\text{m}$  and a maximum diameter of less than about  $2.0\mu\text{m}$ , said abrasive particles being present in said slurry in the amount of about 3% by weight, said water soluble peroxide comprises hydrogen peroxide, said water soluble peroxide being present in said slurry in the amount of up to about 30% by weight, said oxidizing solution further comprises an amino acid and a metal containing compound, said amino acid comprising glycine and being present in said slurry in an amount of up to about 10% by weight, said metal containing compound comprising copper nitrate and being present in said slurry in an amount of up to about 10% by weight.

15. The slurry for chemical-mechanical polishing metal surfaces as in claim 1 wherein said oxidizing solution further comprises organic amine.

16. The slurry for chemical-mechanical polishing metal surfaces as in claim 15 wherein said organic amine is one or more selected from the group consisting of primary amine ( $\text{RNH}_2$ ), secondary amine ( $\text{R}_2\text{NH}$ ), tertiary amine ( $\text{R}_3\text{N}$ ), amines containing all or some



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of these three types of amine moieties, and mixtures thereof, where R is an aliphatic hydrocarbon or an aromatic hydrocarbon.

17. The slurry for chemical-mechanical polishing metal surfaces as in claim 15 wherein said organic amine is present in said slurry in an amount of from about 0.1% to about 10% by weight.

18. The slurry for chemical-mechanical polishing metal surfaces as in claim 15 wherein said oxidizing solution further comprises one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium.

19. The slurry for chemical-mechanical polishing metal surfaces as in claim 15 wherein said abrasive particles comprise alumina having a mean diameter of about  $0.35\mu\text{m}$  and a maximum diameter of less than about  $2.0\mu\text{m}$ , said abrasive particles being present in said slurry in the amount of about 3% by weight, said water soluble peroxide comprises hydrogen peroxide, said water soluble peroxide being present in said slurry in the amount of up to about 30% by weight, said oxidizing solution further comprises an organic amine, said organic amine comprising bis(hexamethylene)triamine and being present in said slurry in an amount of up to about 10% by weight.

20. A method of polishing a metal surface comprising the steps of:

- I. providing a metal surface to be polished;
- II. providing a polishing pad;

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III. contacting said metal surface to be polished with a polishing slurry, said polishing slurry comprising water, abrasive particles and an oxidizing solution comprising one or more water soluble peroxides, said oxidizing solution further comprising either: (a) one or more amino acids and one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium; or (b) one or more organic amines and optionally one or more metals and/or compounds containing metals selected from the group consisting of chromium, cobalt, copper, iron, lead, nickel, palladium, rhodium, samarium, and scandium; and

IV. mechanically polishing said metal surface to be polished using said polishing pad.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/07482

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) :H01L 21/00; B44C 1/22; C09G 1/00 US CL :216/88, 89, 90; 438/692, 693 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 216/88, 89, 90; 438/692, 693 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS Search Terms: chemical mechanical polishing, cmp, metal		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,930,870 A (BASI) 6 January 1976, abstract	12-14
X	US 5,575,885 A (HIRABAYASHI et al) 19 November 1996, Figs. 1 and 2; abstract; col. 2, lines 28-32; col. 4, lines 60-68; col. 5, lines 9-25	1-11, 15-20
X, P	US 5,770,095 A (SASAKI et al) 23 June 1998, Fig. 1; abstract; col. 3, lines 32-35; col. 4, lines 1-10; col. 6, lines 1-12 and 37-45; col. 8, lines 5-20 and 48-49	1-11, 15-20
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 22 JUNE 1999		Date of mailing of the international search report 04 AUG 1999
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